LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

high-temperature phonons in uranium from relativistic first-principles theory

P. Soderlind, B. Grabowski, L. Yang, A. Landa, T. Bjorkman, P. Souvatzis, O. Eriksson

January 5, 2012

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

High-temperature phonons in uranium from relativistic first-principles theory

Per Söderlind, B. Grabowski, L. Yang, and A. Landa

Lawrence Livermore National Laboratory,

Livermore, California 94550, USA

T. Björkman

COMP/Department of Applied Physics,

Aalto University, FI-00076 Aalto, Finland

P. Souvatzis and O. Eriksson

Department of Physics and Astronomy, Division of Materials Theory,

Uppsala University, SE-751210 Uppsala, Sweden

(Dated: January 4, 2012)

Abstract

The phonon dispersion for body-centered cubic (bcc) γ-uranium metal has been calculated from first-principles electronic structure. At low temperatures bcc uranium is mechanically unstable but we show that phonon-phonon interactions stabilize this phase when heated. Utilizing the newly developed self-consistent *ab initio* lattice dynamics (SCAILD) scheme in conjunction with highly accurate and fully relativistic density functional theory we obtain phonon dispersion and density of states that compare well with data acquired from inelastic neutron-scattering experiments. The investigation establishes that the high-temperature dynamical behavior can be computed from *ab initio* even for complex materials with substantial electron-correlation effects such as the actinides metals.

PACS numbers:

Density-functional theory (DFT) [1] has proven to be remarkably successful in describing the $T = 0$ K ground-state phases of most metals in the periodic table of elements. Skriver [2] showed that it predicts the correct ground-state crystal structure for most transition metals when applied in rather rudimentary electronic-structure techniques. Later [3] it became evident that DFT—implemented in more sophisticated methods appropriately treating complex crystal structures—also confirms the ground-state phases of the actinide metals. Except for metals with strong electron-correlation effects, such as the rare-earths, the DFT work horse can nowadays be effectively used throughout the periodic table of elements for *low-temperature* condensed-matter applications.

There has been a long-standing difficulty, however, to model *high-temperature* phases with an accuracy analogous to that of the ground state at room or lower temperatures. The reason is that treating electronic and vibrational properties simultaneously within a quantum-mechanical framework is a daunting task. It becomes particularly problematic when the high-temperature phase is mechanically unstable at low temperatures thus ruling out the typically applied perturbation theory of the zero-temperature electronic structure.

Quantum-mechanical molecular-dynamics methods provide, in principle, the solution to the problem but are feasible only if the electronic structure can be calculated expeditiously enough. Meanwhile, an efficient methodology has been devised that couples DFT forces with temperature-driven atomic displacements (phonons). This self-consistent *ab initio* lattice dynamics (SCAILD) technique [4] has been used to investigate the high-temperature bcc phase of several metals including Ti, Zr, Hf, and even iron [5]. The approach has been described in detail [6] and has heretofore utilized *ab initio* forces obtained from the projector augmented wave (PAW) method in conjunction with the currently most robust PAW implementation, the Vienna *ab initio* simulation package (VASP) [7]. This implementation allows for adept evaluation of the forces required for the SCAILD scheme while being adequately accurate for several transition metals. Here, however, we are concerned with a member of the actinides series, uranium. These heavy metals are more challenging for electronic-structure theory for several reasons. In particular, the presence of narrow $5f$-electron states in the vicinity of the Fermi level strongly destabilizes symmetrical crystal structures, such as cubic or hexagonal, while giving rise to enhanced electron correlation and relativistic effects [8, 9]. PAW calculations for the low-temperature α-uranium phase [10] appear to reproduce all-electron results [11] but for temperatures close to the melting point uranium adopts the bcc

phase and here PAW [10] demonstrates discrepancies of over 40% with all-electron results: The PAW bulk modulus of bcc U from Ref. [10] is 176 GPa whereas the present all-electron calculations give 123 GPa. For comparison, laser-heated diamond anvil cell measurements show a bulk modulus of 113 GPa for bcc U [12]. Although a combination of PAW and spin-orbit (SO) coupling is in principle possible, in practice even the currently most robust PAW implementation yields qualitatively wrong results [10]. Specifically, inclusion of SO coupling lowers the equilibrium volume of bcc U [10], although physically and as confirmed by all-electron calculations [13], it expands the volume. Our own PAW (VASP) calculations including SO coupling similarly do not reproduce the all-electron results (not shown) and we therefore omit them from the following discussion.

Considering the uncertainties regarding the PAW accuracy for uranium, we shift to an electronic structure method which currently—at the expense of computational burden—is the most accurate and therefore most suitable technique for actinide materials: the full-potential linear muffin-tin orbitals (FPLMTO) method. The specific version [14] has been applied successfully to $T = 0$ K properties of actinides in the past [3]. It does not constrain the shapes of the charge density or potential and spin-orbit coupling is included in a first-order variational procedure for the valence d and f states [15], while core states are treated with the fully relativistic Dirac equation. In addition, effects of orbital polarization [16] are examined because of their importance for the neighboring metals Np and Pu [17]. For the electron exchange and correlation we apply the generalized gradient approximation (GGA) and all calculations are conducted at the theoretical (FPLMTO: SO+OP) zero-temperature atomic volume, 20.85 Å^3.

The SCAILD method can be viewed as a generalization of the frozen phonon method [18] and we therefore start with an evaluation of zone-boundary (ZB) phonons applying the frozen-phonon technique. In Table I we show results obtained for two ZB phonons, at the H- and N-point (T_2 branch). At zero temperature both are unstable resulting in imaginary frequencies (shown as negative). Notice first that the FPLMTO results are substantially different than the ones obtained from PAW and that in all cases the all-electron calculations suggest a lesser degree of instability. For instance, the H-point phonon at 300 K (electronic temperature) the PAW frequency is about twice that of the FPLMTO one (both similarly considered without SO coupling). Including SO and OP increases the difference to a consequential factor of 2.5. The same trend holds true also for the T_2 N-point phonon albeit less

3

pronounced. Increasing the electronic temperature to 1200 K (Fermi-Dirac broadening and electronic entropy) diminishes the instability somewhat but does not remove the discrepancy between the methods. Hence, we conclude that even the currently most robust PAW implementation is not suitable for uranium as it significantly overestimates the strength of the bcc instability. In fact, actual SCAILD calculations based on this implementation (details below) fail to correctly stabilize bcc uranium below the melting temperature presumably because the electronic structure is too unstable to be properly counterbalanced by the phonon-phonon interactions provided within SCAILD.

Next, we tackle the high-temperature description of the unstable bcc uranium phase with SCAILD and with our reliable FPLMTO electronic-structure approach. We are faced with two serious challenges: First, the forces in local-basis methods such as FPLMTO are numerically highly difficult to evaluate using a linear-response ansatz (Hellmann-Feynman forces), as opposed to the case of plane-wave techniques. Second, spin-orbit interaction and orbital polarization are practically incompatible with a linear-response force calculation, as the corresponding methodology is currently not thoroughly developed. We are, however, able to circumvent these issues by proceeding in analogy with the frozen-phonon approach. In particular, we choose to extract forces from (electronic) free-energy shifts due to small atomic displacements. The SCAILD scheme requires forces on all atoms in a supercell for which the atoms are thermally displaced from the perfect bcc lattice positions [6]. We obtain forces by independently moving each atom a small ($\pm$ 0.2% of lattice constant) amount along the x, y, and z Cartesian axis, least-square fitting a second order polynomial to the free energies and extracting the force component along the considered axis. Because of the extreme computational effort by the all-electron method and the displacement procedure we limit ourselves to study a 3 x 3 x 3 bcc supercell (27 atoms). A larger cell is of course preferred but our investigation for titanium suggests that using a 27-atom supercell in lieu of a 64-atom cell is reasonable when focusing on the phonon dispersion and density of states.

In Fig. 1 we present calculated titanium phonon dispersions (FPLMTO and PAW) together with neutron-scattering data. In this case we do not expect PAW to be greatly different than any all-electron potential and FPLMTO and PAW are indeed consistent with each other and quite close to the experimental result [19]. The softest branch (Γ-N, T_1), however, is predicted to be somewhat softer than given by neutron scattering [19]. This may not be surprising because it is one of the branches in Ti that are unstable at zero

temperature [4].

The frozen-phonon investigation suggests that the FPLMTO method predicts a less unstable bcc U than that of the PAW (VASP implementation), particularly if relativistic and electron correlations (SO and OP) are accounted for. In Fig. 2 we show the SCAILD phonon dispersions at 500 K for the FPLMTO treatment with (black line) and without (black line solid squares) spin-orbit interaction (including also OP changes the dispersion a small amount, not shown) together with PAW results (red line solid circles). Clearly, PAW gives the strongest unstable dispersions, particularly the Γ-H branch is very negative as a result of too soft H-point phonons. The FPLMTO with SO is still unstable at 500 K but the instability regions are much smaller. The scalar relativistic (noSO) all-electron result is also less unstable suggesting that not only the lack of SO but also an inaccurate PAW potential influences the phonons.

Our main result is the stable phonon dispersion at 1113 K obtained from FPLMTO (SO+OP) free-energy computations coupled with the SCAILD approach. In Fig. 3 this result serves as a prediction since no experimental phonon dispersion exist for γ-U. Armed with this outcome we are able to predict, from first-principles theory, equation-of-state for high-temperature γ-U by constructing a free energy inclusive of the temperature-dependent lattice contributions. In practice the calculations need to be undertaken on a grid of volumes and temperatures so that the phase space is sufficiently sampled. We note that the phonon dispersion is rather insensitive (not shown) to temperature in the 1100-1300 K range which is also consistent with the experimental work [20]. In the absence of a measured γ-U phonon dispersion, we instead compare our calculated phonon density of states with that collected from inelastic neutron-scattering experiments [20] in Fig. 4. The two-peak feature of the measured spectra is clearly reproduced while intensity and location of the high energy peak is identical (no scaling is being applied). The low-energy feature is in slight disagreement as the theoretical DOS is shifted down somewhat and is overall less broad. This could possibly be caused by too soft calculated transverse (T_1) Γ-N phonon branch, in analogy with Ti.

In conclusion, we have successfully calculated high-temperature phonons for a prototype actinide metal (uranium) from relativistic first-principles DFT electronic-structure theory. In spite of being strongly unstable at low temperatures, the vibrational entropy introduced through the SCAILD approach, coupled with forces extracted from FPLMTO free-energy computations, produces a mechanically stable phase with what appears to be a plausible

phonon dispersion. The corresponding phonon density of states agrees satisfactorily with inelastic neutron-scattering experiments, but also reveals that low-energy phonon modes may be underestimated similarly to what was found in Ti, Zr, and Hf [4] suggesting that the SCAILD approach does not include all anharmonicity. We find that for bcc γ-U PAW forces obtained from the currently most robust PAW implementation are not sufficiently accurate to be used in conjunction with SCAILD because these forces overestimate the instabilities. Spin-orbit and orbital-polarization correlations together with an accurate all-electron potential predict a more realistic behavior of γ-U at lower temperatures and are essential for a proper high-temperature description.

We have applied a methodology that circumvents the numerical difficulties of calculating linear-response forces by using free-energy changes due to small atomistic displacements. Hence, one can now use SCAILD for any complex material, for which a realistic energy can be evaluated accurately, such as plutonium metal [21]. We envision to apply this methodology in the near future to study important anomalous temperature-dependent properties for plutonium metal.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).

[2] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).

[3] P. Söderlind, Adv. Phys. **47**, 959 (1998).

[4] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, Phys. Rev. Lett. **100**, 095901 (2008).

[5] W. Luo, B. Johansson, O. Eriksson, S. Arapan, P. Souvatzis, M. I. Katsnelson, and R. Ahuja, PNAS **107**, 9963 (2010).

[6] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, Comput. Matter. Sci. **44**, 888 (2009).

[7] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[8] P. Söderlind, O. Eriksson, B. Johansson, J. M. Wills, and A. M. Boring, Nature **374**, 524 (1995).

[9] P. Söderlind, G. Kotliar, K. Haule, P. M. Oppeneer, and D. Guillaumont, MRS Bull. **35**, 883 (2010).

[10] C. D. Taylor, Phys. Rev. B **77**, 094119 (2008).

[11] P. Söderlind, Phys. Rev. B **66**, 085113 (2002).

[12] C. -S. Yoo, H. Cynn, and P. Söderlind, Phys. Rev. B **57**, 10359 (1998).

[13] M. S. S. Brooks, J. Phys. F **13**, 103 (1983); P. Söderlind, L. Nordström, L. Yongming, and B. Johansson, Phys. Rev. B **42**, 4544 (1990).

[14] J. M. Wills, O. Eriksson, M. Alouani, and D. L. Price, in *Electronic Structure and Physical Properties of Solids*, edited by H. Dreysse (Springer-Verlag, Berlin, 1998), p. 148.

[15] L. Nordström, J. M. Wills, P. H. Andersson, P. Söderlind, O. Eriksson, Phys. Rev. B **63** 035103 (2000).

[16] O. Eriksson, B. Johansson, and M. S. S. Brooks, J. Phys.: Condens. Matter **1**, 4005 (1989).

[17] P. Söderlind, Phys. Rev. B **77**, 085101 (2008); P. Söderlind and A. Gonis, Phys. Rev. B **82**, 033102 (2010).

[18] B. N. Harmon, W. Weber, and D. R. Hamann, Phys. Rev. B **25**, 1109 (1982).

[19] W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, G. Vogl, Phys. Rev. B **43**, 10933 (1991).

[20] M. E. Manley, B. Fultz, R. J. McQueeney, C. M. Brown, W. L. Hults, J. L. Smith, D. J. Thoma, R. Osborn, and J. L. Robertson, Phys. Rev. Lett. **86**, 3076 (2001).

[21] P. Söderlind and B. Sadigh, Phys. Rev. Lett. **92**, 185702 (2004).

Figures

FIG. 1: (Color online). Phonon dispersions for Ti at 1293 K. SCAILD coupled with FPLMTO (black line) and with vasp-PAW (red line solid circles). Experimental data (black squares) are taken from Ref. [19].

FIG. 2: (Color online). Phonon dispersions for γ-U at 500 K. SCAILD coupled with FPLMTO w/o spin-orbit interaction (black line solid squares), with SO (black solid line), and with VASP-PAW (red line solid circles).

FIG. 3: Phonon dispersion for γ-U at 1136 K. SCAILD coupled with FPLMTO (SO+OP) (see main text).

FIG. 4: Phonon density of states for γ-U at 1113 K, calculated (solid line) and inelastic neutron-scattering data (open squares) [20].

Tables

TABLE I: H- and N-point (T_2) zone boundary (ZB) phonons for bcc uranium obtained from the frozen-phonon method [18] and electronic (no vibrational) free energies corresponding to 300 K and 1200 K. Three sets of calculations are performed utilizing the all-electron FPLMTO method w/o (noSO), with spin-orbit coupling (SO), and with orbital polarization (SO+OP). PAW refers to results obtained from projector augmented wave potentials within the VASP implementation (no SO coupling). All frequencies are in units of THz and we adopt the convention to display imaginary (unstable) frequencies as negative.

ZB phonon	noSO	SO	SO+OP	PAW
H (300 K)	-1.14	-0.91	-0.86	-2.03
H (1200 K)	-1.03	-0.68	-0.54	-1.94
N: T_2 (300 K)	-2.28	-2.16	-2.14	-2.64
N: T_2 (1200 K)	-2.17	-2.04	-2.01	-2.55